Sandia National Laboratories

Theoretical Chemical Kinetics and Non-Born–Oppenheimer Chemistry

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Introduction

In the Combustion Chemistry division of the CRF, we study the fundamental chemistry of combustion using a wide variety of experimental and theoretical methods. This poster focuses on our development of new theoretical methods, including

- high-level quantum chemistry calculations
- transition state theory calculations
- master equation calculations
- trajectory simulations

In this poster, we present examples of how we are using these methods to study elementary kinetics and photochemistry.

High-level quantum chemistry

Accurate potential energy surfaces (barrier heights, reaction enthalpies, frequencies) are prerequisites for accurate kinetics. We use a combination of theoretical methods with scalable accuracy and computational cost. Recent work in our laboratory and in collaboration with Klippenstein and Harding at Argonne National Laboratory has demonstrated the improved accuracy of using multireference methods for obtaining geometries and frequencies when single reference methods fail.

Examples: Ethanol combustion

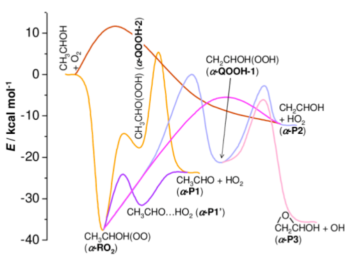


Figure 1. Stationary points on the $CH_3CHOH + O_2$ surface.

High pressure ignition

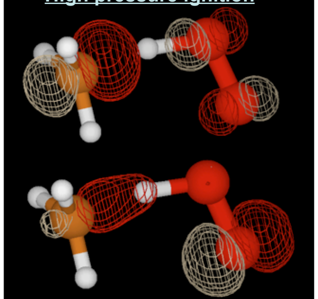


Figure 2. Two a' orbitals with varying occupancies for the multireference $CH_3 + HO_2 \rightarrow CH_4 + O_2$ transition state.

Barrierless kinetics

Barrierless entrance channels are present in many combustion reactions, as shown in figure 1. Barrierless transition states are not well described by traditional methods, such as the rigid rotor and harmonic oscillator (RRHO) approximations. Using Klippenstein's direct variable reaction coordinate transition state theory (VRC-TST), we are able to obtain accurate rates for these processes.

Examples: Methanol decomposition

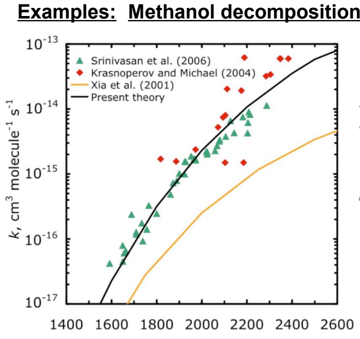


Figure 3. CH_3OH low pressure decomposition rates.

CH_3 + OH

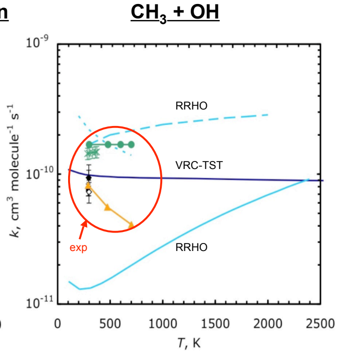


Figure 4. CH_3+OH high pressure association rates.

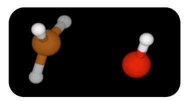
Phenomenological rate coefficients from the multiple-well master equation

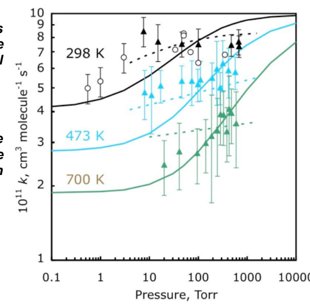
Master equation methods developed at the CRF in collaboration with Klippenstein allow for the accurate determination of the often complicated temperature and pressure dependence of rates for reactions occurring over multiple wells and with multiple product channels. These types of reactions are common in combustion due to the significance of radical species and molecular rearrangements.

Figure 5. Pressure and temperature dependent rates for CH_3 + OH. The theoretical results (solid lines) are in excellent agreement with the experimental measurements (symbols).

Previous fits to the experimental data are shown as dashed lines.

The theory suggests a reinterpretation of the experimental results, predicting more pressure dependence and less temperature dependence than the original experimental interpretation.





Energy transfer parameters from trajectories

For many systems, the dominant source of uncertainty in the master equation calculations is the treatment of collisional energy transfer, which accounts for the activation and stabilization of the intermediate complexes. We have shown that direct classical trajectories can be used to predict these parameters accurately.

Figure 6. Trends in energy transfer for CH_4

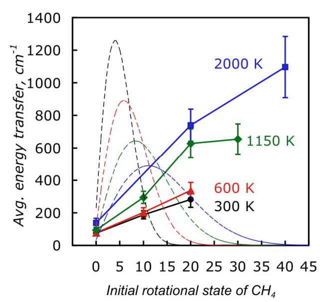
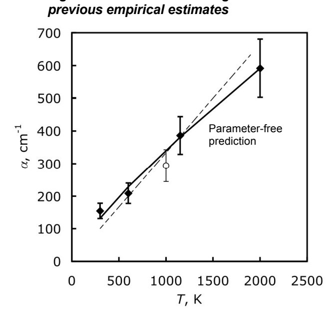


Figure 7. Predicted values agree well with previous empirical estimates



Non-Born–Oppenheimer molecular dynamics

Trajectory-based (classical) methods for dynamics are useful for elucidating reaction mechanisms, identifying important product species, modeling energy transfer, and simulating ensembles.

We are extending these methods to include important quantum effects, such as electronic state transitions and electronic coherence. These NBO MD methods are useful for studying photochemistry (relevant to laser diagnostics) and spin-forbidden processes in combustion.

We are validating our methods on well-characterized systems such as NH_3, which has a conical intersection for fast excited state decay, and NaFH, which demonstrates the harpooning mechanism.

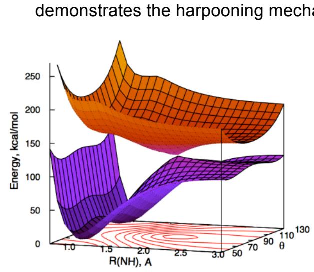


Figure 8. Coupled X and A states of NH_3

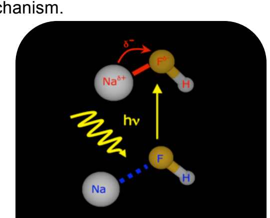


Figure 9. Harpooning. Upon photoexcitation, charge density is transferred from the Na atom to the F atom, thus strengthening the NaF bond, weakening the HF bond, and enhancing the likelihood of the system fragmenting to the NaF + H products.

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